

Gas-Phase Molecules Illuminated from Within

Seeing is believing, and the importance of visualization is obvious at the molecular level, which lies outside the realm of everyday experience. Gas-phase molecules, however, present some difficulties because traditional techniques for probing within molecules, such as photoelectron diffraction, require knowledge of the molecule's orientation. Addressing this problem, an international collaboration of researchers has demonstrated a multi-particle coincidence technique at the ALS that yields comprehensive photoelectron diffraction data for gaseous carbon monoxide as if the molecules were fixed in space. The most striking aspect of viewing molecules "illuminated" from within this way is how the results reveal, nearly at a glance, the major physical features at play.

In x-ray photoelectron diffraction (XPD), a core-level electron is ejected from one atom in a molecule by an incoming x ray. The ejected photoelectron wave, diffracted by neighboring atoms, provides a signature of the nonspherical potential of

the molecule. However, to fully observe the rich, three-dimensional structure of the electron wave, knowledge of the orientation of the molecule is required. In most cases, the material under investigation is in solid form (crystal or adsorbate) and can be easily oriented in the laboratory. Determining the orientation of a freely moving molecule, however, requires some experimental finesse.

At Beamline 9.3.2, a beam of CO gas can be crossed with a beam of linearly polarized x rays. This removes the C 1s electron and leaves the molecule in a highly excited state. The molecule then rapidly dissociates into C and O positive ions. The fragments (ions and electrons) are drawn by electric and magnetic fields toward position-sensitive detectors. Only triple coincidences between two ions and one electron are recorded. From the times of flight and the impact positions, the momenta of all particles in all directions are calculated. Because the dissociation time of ionized CO is substantially shorter than its rota-

tion period, measurement of the C and O momentum vectors gives the molecule's orientation upon photoionization. In contrast to previous experiments, this technique records, with high efficiency and resolution, the full picture of the outgoing electron wave for all orientations of the molecule simultaneously. One can, by computer analysis, select and organize the results to show the electron emission pattern as if all the molecules were oriented in the same way; the researcher simply chooses how to view the process and sorts the data accordingly.

For example, the data can be displayed in a map of the photoelectron momentum vectors, where the azimuthal angle gives the direction of the photoelectron emission, the radial distance gives the photoelectron energy, and the emission intensity is indicated by color. The resulting pictures are rich in physics: one sees the outgoing wave resonating in the molecular potential at a certain energy (i.e., at a constant radius) and displaying interference from reflection off of the oxygen

partner ("bright" spot when the molecular axis is aligned with the x-ray polarization ϵ). An alternative depiction, in polar coordinates, lets us compare the experimental photoelectron momentum data to calculations based on linear combinations of partial waves. The high fidelity of the fitted curves to the data demonstrates that the contributions of different partial waves to the photoelectron wave can be successfully extracted from the data.

While the researchers chose a simple ground-state molecule for this demonstration, the technique might also be used to produce time-dependent snapshots of transient species. It may be possible to map the evolution of molecular potentials by initiating a photochemical reaction with a short laser pulse and later probing the molecule using a photoelectron wave generated by a time-delayed x-ray pulse. Thus, this approach to viewing molecules is a major step forward in our ability to obtain comprehensive information about molecular dynamics and structure from photoelectron emission. ■

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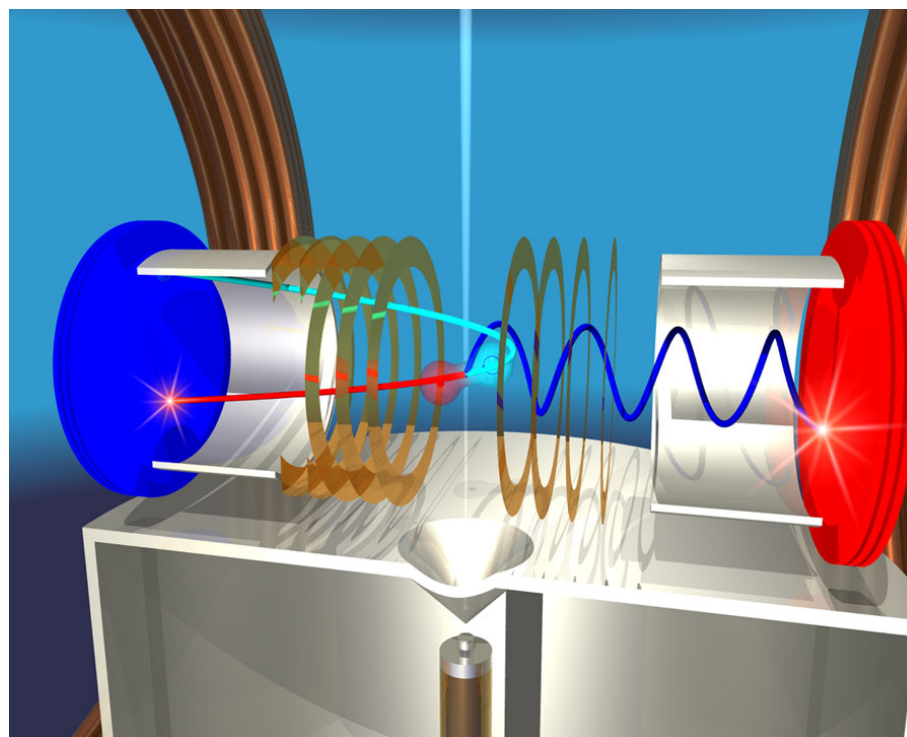
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PHOTOELECTRON DIFFRACTION MAPPING

Gas-Phase Molecules Illuminated from Within

- **X-ray photoelectron diffraction (XPD): signature of molecular potential**
 - *Requires knowledge of molecular orientation; traditionally performed on solid materials*
 - *Previous work on gas molecules yielded incomplete pictures of photoelectron distributions*
- **Multiparticle coincidence technique at ALS Beamline 9.3.2**
 - *Supersonic jet of CO gas*
 - *Linearly polarized x rays*
 - *CO ionizes (e^-), dissociates (C, O)*
 - *Triple coincidences recorded*
 - *Reconstruct molecular orientation*
- **Comprehensive 3-D images**
 - *Full picture of outgoing electron wave*
 - *Pattern evolves as molecule rotates*
 - *High resolution and efficiency*
- **Future application**
 - *Evolution of photochemical reactions*
 - *“Snapshots” of molecular potential*
 - *Temporal and spatial resolution*



PHOTOELECTRON DIFFRACTION MAPPING

Gas-Phase Molecules Illuminated from Within

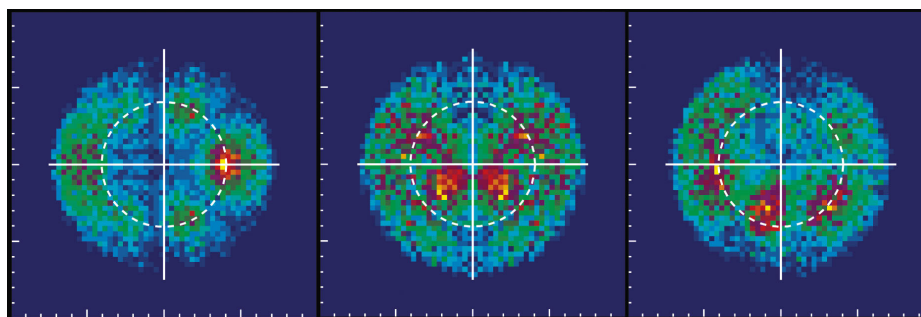
Momentum distributions

Azimuthal angle = Emission direction

Color = Emission intensity

Radius = Photoelectron energy

● = carbon
● = oxygen
 ε = x-ray polarization



Polar coordinates

Data for 10.2-eV photoelectrons
(i.e., dashed circles in series shown
above) compared to fitted partial
wave expansions (solid curves).

